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June 12, 1990

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

For

Grant/Contract N00014-89-J-3063

R & T Code 4132041

Processing of Polymers Using Supercritical Fluids

John J. Aklonis and Eric J. Amis, Principal Investigators

Department of Chemistry
University of Southern California
University Park
Los Angeles, CA 90089-1661

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PART I

- a. Papers Submitted to Refereed Journals: A. M. Espinoza and J. J. Aklonis, "Memory Experiments in Physically Aging Systems: A Test of Multiordering Parameter Models", *Thermochim. Acta*, in press.
- b. Papers Published in Refereed Journals: A. M. Espinoza and J. J. Aklonis, *Proc. 18th N. Amer. Ther. Anal. Soc. Conf.*, Vol. 1, (1989), 26.
- c. Books Submitted for Publication: none
- d. Books Published: none
- e. Technical Reports Published (including ONR Technical Report) and Papers Published in Non-Refereed Journals: A. M. Espinoza and J. J. Aklonis, *Bull. Amer. Phys. Soc.*, v. 35, 508 (1990).
- f. Patents Filed: none
- g. Patents Granted: none
- h. Invited Presentations at Topical or Society Conferences:
 - (i) J. J. Aklonis, "Physical Aging of Polymers", Mobil Chemical Co., Edison, N.J., September 17, 1989.
 - (II) J. J. Aklonis, "Memory Experiments in Physically Aging Systems: A Test of Multiordering Parameter Models", North American Thermal Analysis Society, San Diego, CA, September 24, 1989.
 - (III) J. J. Aklonis, "Kinetics of the Glass Transition and Multiordering Parameter Models", American Institute of Chemical Engineers National Meeting, San Francisco, November 9, 1989.
 - (IV) "Aging of Polymer Glasses", Symposium Honoring J. D. Ferry, Loker Hydrocarbon Research Institute, U.S.C., Los Angeles, CA, March 8, 1990.
 - (V) J. J. Aklonis, "Kinetic Aspects of the Glass Transition and Physical Aging in Glasses", Marshall Labs, DuPont Company, Philadelphia, PA, April 30, 1990.
 - (VI) J. J. Aklonis, "Aging of Polymer Glasses", Polymer Products, DuPont Company, Wilmington, DE, May 1, 1990.
- i. Contributed Presentations at Topical or Scientific/Technical Society Conferences: none
- j. Honors/Awards/Prizes: John J. Aklonis, Raubenheimer Award, University of Southern California, May 15, 1990.
- k. Number of Graduate Students Receiving at least 25% Support on ONR Grant or Contract:

Total 2

Minorities 2

Asian 1

- l. Number of Postdoctoral Fellows Receiving at least 25% Support on ONR Grant or Contract:

Total 2 Minorities 2 Asian 2

- m. Other Funding: Office of Naval Research, Grant/Contract N00014-88-K-0302, R & T Code 413m010, "The Behavior of Polymers Filled With Monodisperse Polymer Beads", R. Salovey and J. J. Aklonis, Chemistry Department, USC, \$1,073,281 total for 36 months, May 1, 1988 to April 30, 1991.

PART II

- a. John J. Aklonis/Eric J. Amis
b. 213-743-2793/213-743-6913
c. Jo Ann Milliken and Kenneth Wynne
d. Brief Description of Project:

In the past, most of the effort expended in the area of supercritical fluids and polymers has been devoted to chromatography and separation. We propose to explore using supercritical fluids as solvents for the preparation of polymers and polymer blends in the form of fibers, polymer sheets and perhaps irregularly shaped polymer solids. It is well known that many of the most interesting new "high tech" polymers are exceedingly difficult to fabricate. These polymers exhibit such highly desirable properties as electrical conductivity, extremely high strength or remarkable thermal stability to name but a few. In the supercritical regime, one can vary and control the "solvent power" of fluids over ranges much broader than those accessible in the usual liquid regime. We are attempting to take advantage of the high variability of solvent power of supercritical fluids with respect to processing of homopolymers as well as making polymer blends with unique properties. *Keywords: Processing of Polymers, Supercritical Fluids, Solvents, Light Scattering Studies, PMMA*

- e. Significant Results During the Last Year:

In our first nine or so months of work, we have set up the apparatus necessary to measure phase diagrams of polymers in supercritical fluids and have proceeded to measure the solubilities of several "garden variety" polymers in various supercritical fluids. We have learned that this project is much more difficult than we had originally anticipated since there are few fluids whose supercritical regimes occur at temperatures low enough to prevent severe degradation of the polymers under study. Our work has concentrated on polymer/supercritical fluid systems where this is not a problem.

- f. Plans For The Next Years Work.

f. Plans For The Next Years Work.

Now that we know some of the limitations which we are facing, we are in a position to make considerable progress. In our initial work, we have discovered polymer/supercritical fluid systems which are suitable for fabrication studies. We now will explore making fibers and films based on these systems. We also intend to shift our emphasis away from "garden variety" polymers to more exotic, in particular high temperature stability, polymers. This change in emphasis will greatly expand the range of solvents which can be used as supercritical fluids. We anticipate that this change in emphasis will greatly accelerate our progress.

In addition to studying fabrication, we will carry out some of the first static and dynamic light scattering studies of molecules dissolved in supercritical fluids. Although this is very difficult research, we have high expectations for success since, except for the fabrication of an appropriate light scattering cell, all of the laser facilities, computer hardware and software and know-how, are currently operational in our laboratories. In addition, we are constructing a device which will allow us to measure the viscosity of polymers in supercritical fluid solution using a magnetic sphere technique. Now that we better understand problems associated with treating polymers in supercritical fluids, we are in good shape to launch these studies.

- g. Prof. Lizhui Gan (Visiting Scholar)
Dr. Marian Sedlak
Mr. Ming Hu
Mr. Abel Espinoza
Ms. Sylvia Law



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PART III

Processing of Polymers Using Supercritical Fluids

Solvating Power depends strongly on density.

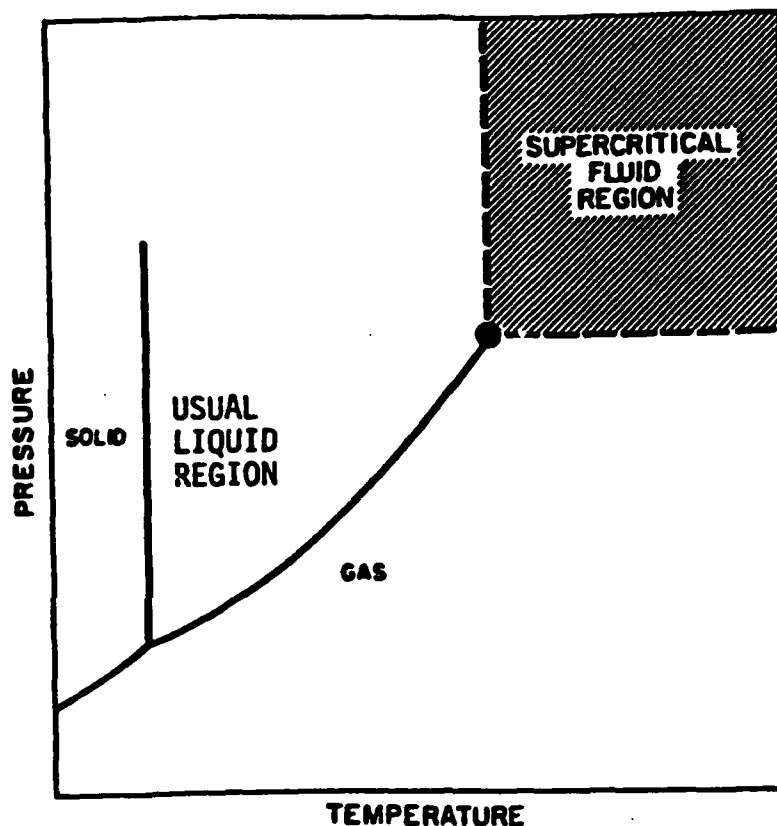


Figure 1.1 Pressure-temperature diagram for a pure component.

In the "Usual Liquid Region" the density is essentially constant.

In the "Supercritical Fluid Region", the density can be varied widely which allows the solvating power to be "tuned".

Figure 1

**Apparent Solubility of High Molecular
Weight PMMA in a Supercritical
Pentane/Ethylacetate Solution at 214 °C**

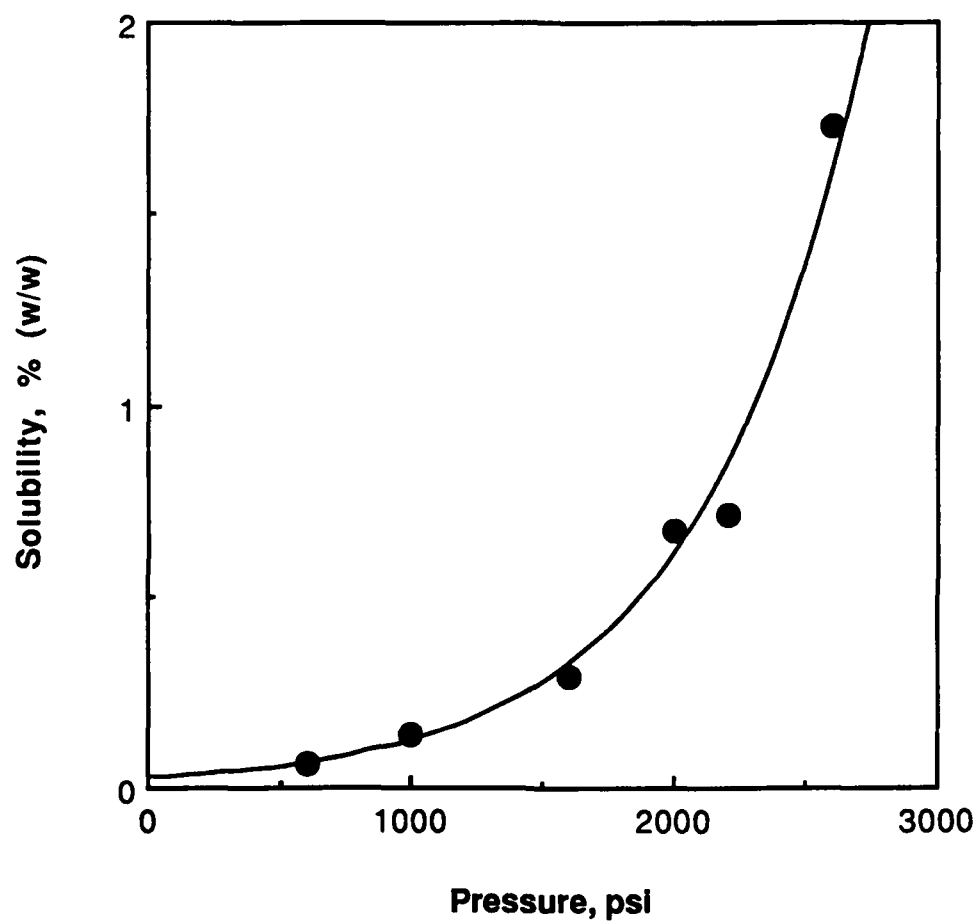


Figure 2

Some of the Approaches to be Explored

- a) Rapid Expansion of Supercritical Fluid Solutions. (RESS)
Matson, et. al., Ind. Eng. Chem. Res., 26, 2298 (1987).**
- b) Precipitation induced by pressure and/or temperature variations.**
- c) Precipitation induced by addition of non-solvent.**
- d) Precipitation induced by polymer composition changes caused
by chemical reactions occurring under SCF conditions.**
- e) Fiber formation using modified spinnerette techniques.**
- f) Film formation using modified extrusion techniques.**

Explanatory Material

Under ordinary conditions, the solubility of a substance such as a polymer in a simple fluid at a certain temperature is a constant. Fundamentally, this situation results from the fact that liquid densities are fixed at fixed temperatures and, since density is a (the?) major parameter in determining solvent quality in a particular solvent, the solubility is also fixed.

In the supercritical regime, Figure (1), the density of a fluid can be varied over wide ranges at constant temperature through pressure variations. Thus gas-like, as well as liquid-like densities are accessible as are all densities in between these two extremes.

The importance of such density variations in influencing solubility is made clear in Figure 2. Here we have measured the "apparent" solubility of a reasonably high molecular weight PMMA in a mixed solvent of pentane and ethylacetate in the supercritical regime just above 200° C. Our data indicates that the solubility varies by about a factor of 30 over the easily accessible pressure range of 600 to 2600 PSI. This enormous variability of solubility is to be contrasted with the fixed solubility of this PMMA sample in liquid pentane/ethylacetate.

Processing often involves precipitation or deposition of polymeric materials from solutions. We are exploring using the control of solubility which exists in supercritical fluid solutions to treat difficult to process polymers and to make blends of polymers which may have unusual properties.

*The adjective "apparent" is used since there is undoubtedly a fractionation taking place in the solution process. We have found that low molecular weight polymers are much more soluble than high molecular weight polymers and there is surely an influence of this factor in the data. We are currently investigating the importance of this effect.